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Study on the Reduction Process of Vanadium Oxide Catalysts by Means of Infrared Spectroscopy and X-ray Diffraction

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By x-ray diffraction and infrared spectroscopy, the changes of the structures of V_2O_5, V_2O_5-25% MoO_3 and V_2O_5-7% WO_3, respectively, were investigated in the course of reduction with cyclohexane or NH_3.

V_2O_5-catalysts were reduced to V_2O_4 via $V_2O_5+V_2O_4$ and $V_{12}O_{26}$ under the mild conditions.

The doping MoO_3 or WO_3 into V_2O_5 in the range of the formation of the solid solution caused the increase in the reducibility of the catalyst and in the stability of the crystal structure of V_2O_5, simultaneously.

INTRODUCTION

The reduction process of vanadium (V) oxide (V_2O_5) has been already studied by a number of researchers. In the previous work[1], it was observed that V_2O_5 was directly reduced to V_2O_3 with H_2 at temperatures above 500°C, but reduced to V_2O_3 via $V_{12}O_{26}$ with SO_2 or NH_3, and the V_2O_5-MoO_3 was more easily reduced than V_2O_5 with C_6H_6 at temperatures below 300°C.[2,3] Simard *et al.*[4] investigated the composition of V_2O_5 catalyst during oxidation of o-xylene and recognized that the composition of catalyst as a function of catalyst bed depth varied to $V_{12}O_{26}$, V_2O_4 and V_2O_3. Matsuura[5] observed microscopically the colour change of V_2O_5 crystal in the course of reduction with H_2, and clarified that after the surface was covered with reduced layer of V_2O_3, reduction into the bulk phase of the crystal proceeded. Recently, such new compounds as V_3O_7[6], V_4O_9[7] and two kinds of $V_{12}O_{26}$[8] were found in the reduction process of V_2O_5 by means of x-ray diffraction.

In the present work, x-ray diffraction and infrared spectroscopy were adopted to elucidate the changes of the crystal structure and of the state of the V=O bond of powdered V_2O_5, V_2O_5-25% MoO_3 and V_2O_5-7% WO_3, respectively, in the course of reduction with cyclohexane (C_6H_{12}) or NH_3 under relatively mild conditions.

EXPERIMENTAL

1. Materials

a) V_2O_5-sample was prepared by the calcination of NH_4VO_3 (extrapure grade) at 450°C for 6 hr in dry air stream.

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b) Sample of V_2O_5-25% MoO_3 was prepared as follows. V_2O_5 given above and MoO_3, which was obtained from chemical pure grade $(NH_4)_6Mo_7O_{27}$ in the same way as V_2O_5, were mixed in the molar ratio of 3 : 1, melted together at 700°C for 30 min in a quartz crucible, allowed to cool in the furnace, and the solidified sample was ground to powder of about 200 meshes.

c) Sample of V_2O_5-7% WO_3 was prepared in the similar way as V_2O_5-MoO_3 sample. WO_3 was obtained from chemical pure grade $(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$.

d) C_6H_{12} (extrapure grade cyclohexane) which was dried over metallic Na was further purified by distillation.

e) NH_3-gas from commercial cylinder was dried over anhydrous silica gel before use.

2. Apparatus and Procedure

a) Reduction with C_6H_{12}. The catalyst-samples (300-500 mg) were charged with 30 cc of liquid C_6H_{12} in an autoclave and were treated in the range of temperatures of 80°C to 400°C for 5 hr in the N_2 atmosphere.

b) Reduction with NH_3. The samples were reduced in a stream of NH_3 gas in a pyrex glass tube heated at 300°C-400°C. The conditions of reduction are summarized in Table 1.

Table 1. The conditions of reduction.

V_2O_5			V_2O_5-25 mol % MoO_3			V_2O_5-7 mol % WO_3		
Samples	Temperature (°C)	Duration	Samples	Temperature (°C)	Duration	Samples	Temperature (°C)	Duration
V-C-1	102	5 hr	M-C-1	80	5 hr	W-C-1	150	5 hr
V-C-2	130	〃	M-C-2	100	〃	W-C-2	200	〃
V-C-3	176	〃	M-C-3	144	〃	W-C-3	250	〃
V-C-4	204	〃	M-C-4	220	〃	W-C-4	300	〃
V-C-5	262	〃	M-C-5	280	〃	W-C-5	400	〃
			M-C-6	300	〃			
			M-C-7	400	〃			
V-N-1	300	10 min	M-N-1	350	15 min	W-N-1	350	15 min
V-N-2	350	15 min	M-N-2	〃	1 hr	W-N-2	〃	1 hr
V-N-3	〃	1 hr	M-N-3	400	〃	W-N-3	400	〃
V-N-4	400	〃						

All C series samples were reduced with cyclohexane.
All N series samples were reduced with ammonia.

c) X-ray diffraction. A diffractometer of GX-111B type by the Shimadzu Co. Ltd. was used. Measurements were carried out at room temperature using Cu-target.

d) Infrared spectroscopy. A Shimadzu IR-27 type spectrometer was used. Absorption spectra for the samples suspended in Nujol were recorded in the range of wave number of 600 cm^{-1} to 1200 cm^{-1}, by using NaCl-cell.

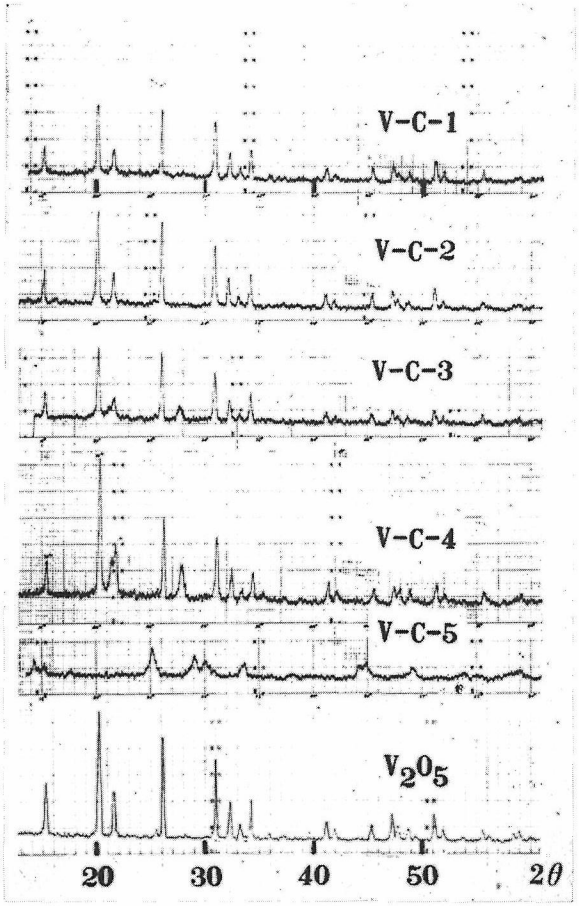
EXPERIMENTAL RESULTS

1. Colour Change of Catalyst in the Course of Reduction

V_2O_5-sample was initially orange yellow, but in proceeding of reduction with C_6H_{12} or NH_3, its colour changed to dark blue through brown. Such the colour change in the course of reduction is expectable from the previous observation by chemical and x-ray analyses that V_2O_5 (orange yellow) was reduced to V_2O_4 (blue black) via $V_{12}O_{26}$ (dark blue) with SO_2 or NH_3 at temperatures below 400°C.[1] V_2O_5-MoO_3 sample was initially green, because this contained about 6% of V^{4+}[9] and its colour changed to dark blue through dark green by reduction. In the case of V_2O_5-WO_3 sample which contained about 2% of V^{4+}[10], its colour changed from brown to dark blue.

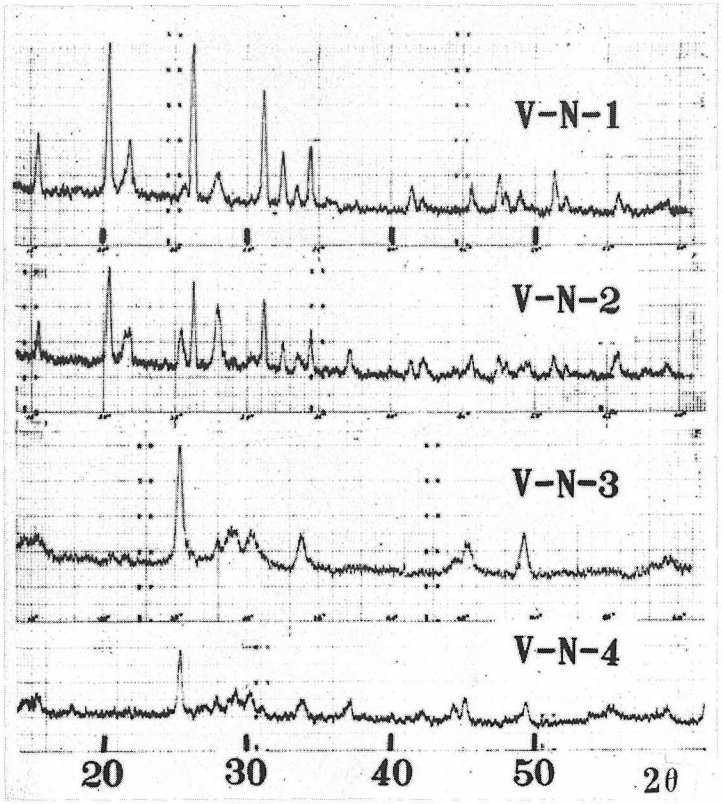
2. X-ray Diffraction

a) V_2O_5: The x-ray diffraction patterns of the samples reduced with C_6H_{12} (V-C series) are shown in Fig. 1. No structural change from V_2O_5 was observed



Diffraction angle (degree)

Fig. 1. X-ray diffraction patterns of V-C series.



Diffraction angle (degree)

Fig. 2. X-ray diffraction patterns of V-N series.

Table 2. The changes of the crystal structures.

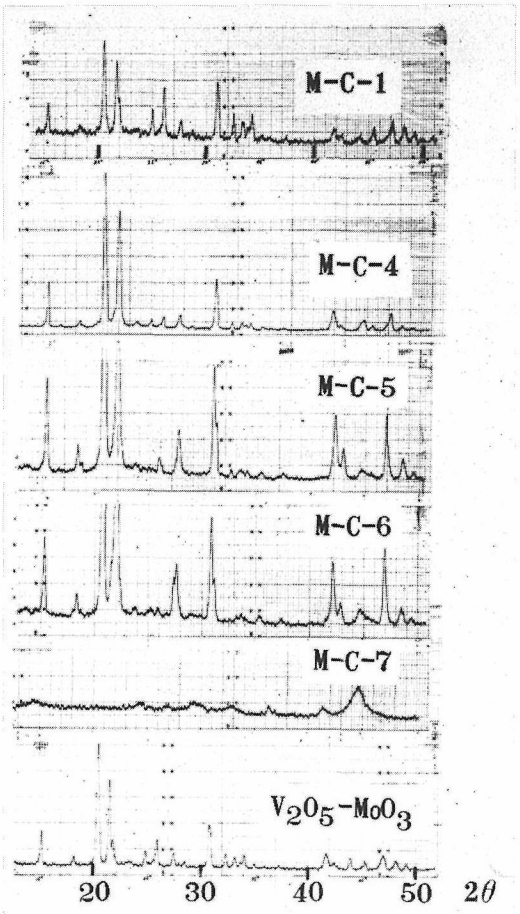
Temp. ℃	A		B		C	
		V_2O_5		V_2O_5-25% MoO_3		V_2O_5-7% WO_3
			M-C-1	V_2O_5		
	V-C-1	V_2O_5	M-C-2	V_2O_5		
100						
	V-C-2	V_2O_5	M-C-3	V_2O_5	W-C-1	V_2O_5
	V-C-3	$V_2O_5+V_2O_4$ (t)				
	V-C-4	$V_2O_5+V_2O_4$ (s)			W-C-1	V_2O_5
200						
			M-C-4	V_2O_5	W-C-3	$V_2O_5+V_2O_4$ (t)
	V-C-5	$V_{12}O_{26}$	M-C-5	$V_2O_5+V_2O_4$ (s)		
			M-C-6	$V_2O_5+V_2O_4$ (s) $+V_{12}O_{26}$ (t)	W-C-4	$V_2O_5+V_{12}O_{26}$ (s)
300						
			M-C-7	V_2O_3+(?)	W-C-5	$V_{12}O_{26}+$(?)
400						
	V-N-1	$V_2O_5+V_2O_4$ (s)				
300						
	V-N-2	$V_2O_5+V_2O_4$	M-N-1	$V_2O_5+V_2O_4$ (t)	W-N-1	$V_2O_5+V_2O_4$ (t)
350						
	V-N-3	$V_{12}O_{26}$	M-N-2	$V_2O_5+V_{12}O_{26}$ (t)	W-N-2	$V_2O_4+V_2O_5$ $+V_{12}O_{26}$ (s)
	V-N-4	$V_2O_4+V_{12}O_{26}$	M-N-3	$V_{12}O_{26}+V_2O_4$	W-N-3	$V_{12}O_{26}+V_2O_4$ (s)
400						

s: small amount t: trace

for V-C-1 and V-C-2 which were treated at temperatures below 130°C. In the case of V-C-3 and V-C-4, weak diffraction lines at d=3.20, 2.13 and 1.65 (2θ=27.8, 42.4 and 55.7) appeared additionally. These lines correspond to the three strong lines of V_2O_4.[11] V-C-5 reduced at 262°C showed a remarkably different pattern from those of V_2O_5 and V_2O_4. This pattern corresponds completely with that of the compound which was identified as $V_{12}O_{26}$ previously.[1] The x-ray diffraction patterns of samples reduced with NH_3 (V-N series) are shown in Fig. 2. The patterns of V-N-1 and V-N-2, which were reduced at temperatures below 350°C for 15 min, were mainly composed of that of V_2O_5 and contained additionally some diffraction lines corresponding to that of V_2O_4. The pattern of V-N-3 reduced at 350°C for 1 hr was similar to that of $V_{12}O_{26}$ observed in V-C-5. In the case of V-N-4 reduced at 400°C, the four strong lines of V_2O_4 (2θ=27.9, 37.2, 42.1 and 55.5) were observed besides that of $V_{12}O_{26}$.

These results show that the crystal structure of V_2O_5-samples varies with reduction under the relatively mild condition as listed in Table 2 (column A).

b) V_2O_5-MoO_3 : Figure 3 shows the diffraction patterns of the samples reduced

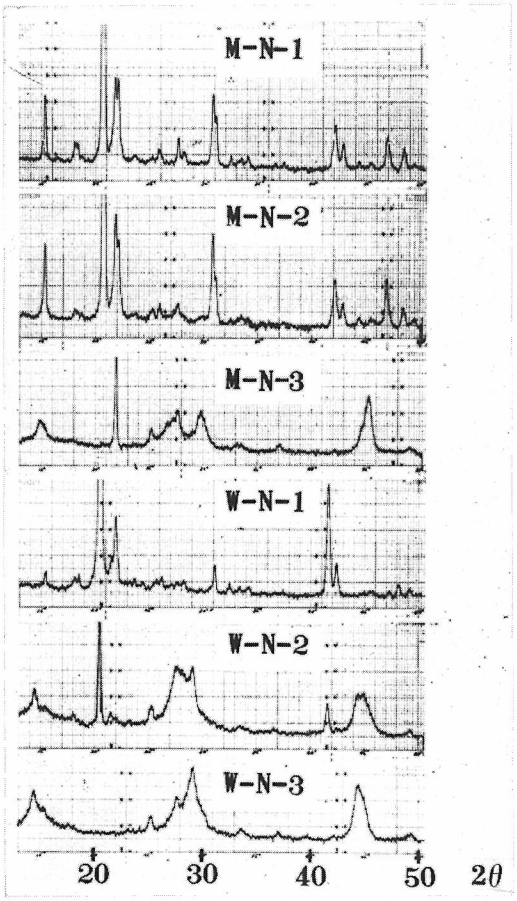


Diffraction angle (degree)

Fig. 3. X-ray diffraction patterns of M-C series.

with C_6H_{12} (M-C series). The V_2O_5-25% MoO_3 gave the similar diffraction pattern to that of V_2O_5 as reported previously.[12] This fact shows that the sample is a solid solution of V_2O_5 and MoO_3, and has almost same crystal structure as that of V_2O_5. No structural change was observed in the sample M-C-1 to M-C-4 which were reduced at temperatures below 220°C. In the diffraction pattern of M-C-5 reduced at 280°C, a strong line at $2\theta=27.7$ and a very weak line at $2\theta=37.3$ could be observed. This means the structure of this sample changed partially to the similar one to that of V_2O_4. The M-C-6 sample reduced at 300°C gave the diffraction pattern which composed of somewhat stronger lines of V_2O_4-structure than that of M-C-5 and of additional weak lines corresponding to $V_{12}O_{26}$-structure ($2\theta=$ 25.0 and 33.7). But even in the cases of both samples of M-C-5 and M-C-6, the main crystal structure was similar to that of V_2O_5. M-C-7 reduced at 400°C gave a remarkably different pattern, some lines of which could be ascribed to that of V_2O_3-structure[11] ($2\theta=24.5$, 33.0 and 36.2) but another lines could not be yet assigned.

As shown in Fig. 4, the pattern of M-N-2 which were reduced with NH_3 at 350°C were mainly composed of similar one to that of V_2O_5, but the former con-



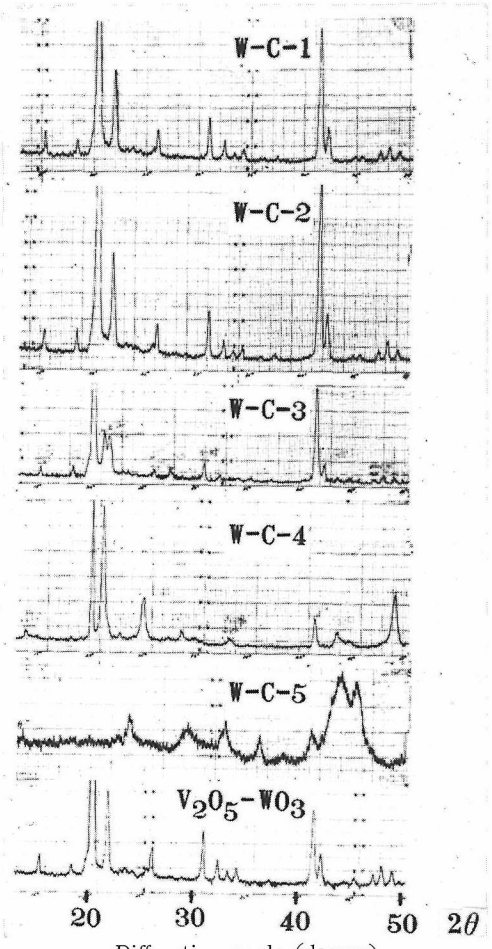
Diffraction angle (degree)

Fig. 4. X-ray diffraction patterns of M-N and W-N series.

tained an additional weak line ($2\theta=28.0$) probably belonging to V_2O_4-structure, while the latter contained weak lines belonging to $V_{12}O_{26}$- and V_2O_4- structures. In the pattern of M-N-3 reduced at 400°C, the diffraction lines of $V_{12}O_{26}$- and V_2O_4- structures were observed with about equal intensity.

In Table 2 (column B), the changes of the crystal phases in the reduction process of V_2O_5-MoO_3 catalysts are summarized.

c) V_2O_5-WO_3 : The x-ray diffraction patterns of samples of W-C series are shown in Fig. 5. The starting sample which contained 7 mol % of WO_3 gave the characteristic x-ray diffraction pattern of V_2O_5-structure as in the case of V_2O_5-MoO_3 samples. W-C-1 and W-C-2 samples which were reduced at temperatures below 200°C, did not show any structural change from the starting sample. In the diffraction pattern of W-C-3 sample reduced at 250°C, a line corresponding to the strongest line of V_2O_4 appeared additionally. The diffraction pattern of W-C-4 sample reduced at 300°C was composed of the pattern of $V_{12}O_{26}$-structure ($2\theta=$ 14.3, 25.3, 30.3, 33.6, 43.8 and 45.0) and that of V_2O_5-structure. A remarkably



Diffraction angle (degree)

Fig. 5. X-ray diffraction patterns of W-C series.

different pattern was observed for W-C-5 sample reduced at 400°C. In this pattern, diffraction lines corresponding to those of $V_{12}O_{26}$-structure were observed besides two strong lines ($2\theta=45.0$ and 46.5) which could not be yet assigned.

The diffraction patterns of W-N series samples are shown in Fig. 4. W-N-1 sample which was reduced at 350°C for 15 min, almost retained the V_2O_5-structure with very small portion of V_2O_4-structure. The structure of W-N-2 reduced at 350°C for 1 hr was mainly V_2O_4-structure and partially V_2O_5- and $V_{12}O_{26}$-structure. The pattern of W-N-3 mainly composed of diffraction lines of $V_{12}O_{26}$-structure besides weak lines of V_2O_4-structure. In Table 2 (column C), the changes of the crystal phases of W-C and W-N series samples are summarized.

3. Infrared Spectra

a) V_2O_5: The infrared spectrum of V_2O_5 has two characteristic absorption bands at 1025 cm^{-1} and 830 cm^{-1}. The former band is relatively sharp one due to the stretching vibration of the $(V=O)^{3+}$ bond and the latter band is broad one arised probably from the V-O-V bond.[13]

Figure 6 shows the infrared spectra of the samples of V-C series. In this figure, it is apparently observed that the characteristic band of the V=O bond was retained in the samples which were reduced with C_6H_{12} at temperatures below 204°C, but in the spectrum of M-C-7, this band diminished. (An absorption band

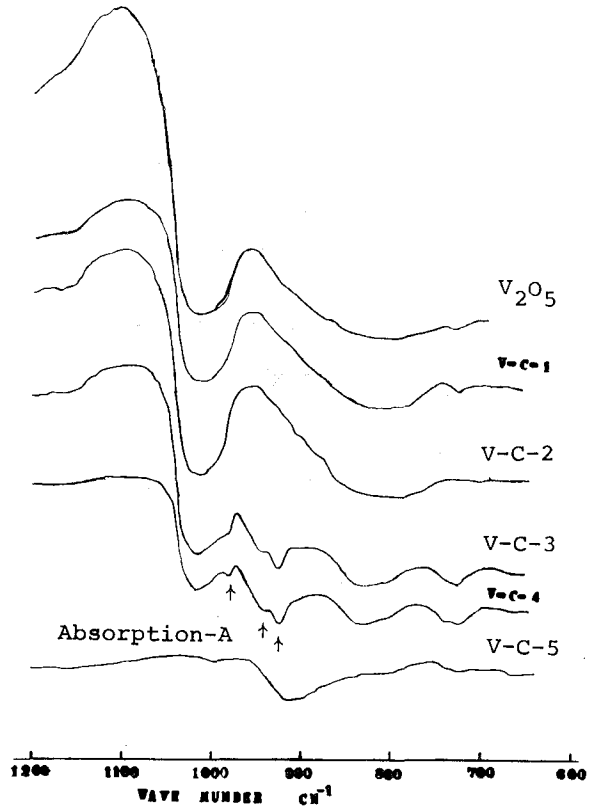


Fig. 6. Infrared absorption spectra of V-C series.

at 720 cm^{-1} is resulted from Nujol.) The spectra of V-C-3 and V-C-4 had several new bands (absorption A in Fig. 6) which are very resemble to that of V_2O_4 reported by Frederickson.[14]

The infrared spectra of samples of V-N series are shown in Fig. 7, and the spectra of V-N-1 and V-N-2 retained the V=O bond, but in the cases of V-N-3 and V-N-4, no V=0 bond was observed.

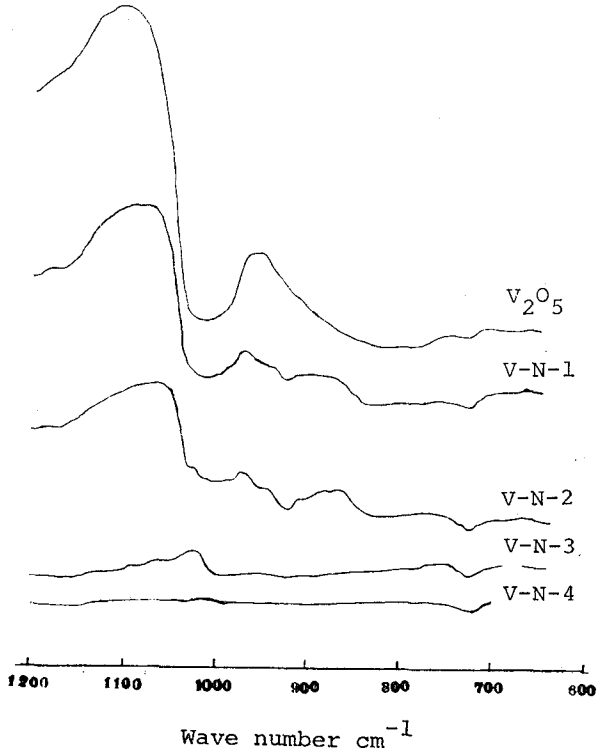


Fig. 7. Infrared absorption spectra of V-N series.

b) V_2O_5-MoO_3: The infrared spectrum of this sample was similar to that of V_2O_5, but the absorption peak at 1025 cm^{-1} shifted to a longer wave length and became broader as the results of increase of V^{4+} ions.[12] Figure 8 shows infrared spectra of M-C series. The characteristic band due to the V=O bond was observed in the spectra of the samples from M-C-1 to M-C-5 and in the infrared spectra of M-C-4 and M-C-5, absorption A appeared. Furthermore, in the case of M-C-6, another new broad band at 920 cm^{-1} (absorption B in Fig. 8) was observed. This broad band is probably associated with $V_{12}O_{26}$-structure in comparison with the result of x-ray analysis. The infrared spectrum of M-N-1 composed of characteristic band due to the V=0 bond and absorption A, but M-N-2 and M-N-3 did not show any clear absorption band (Fig. 9).

c) V_2O_5-WO_3: As shown in Fig. 9 and 10, the infrared spectra of V_2O_5-WO_3 changed by reduction in a similar manner as V_2O_5-MoO_3. But in this case, the V=O bond diminished by milder reduction than in the case of V_2O_5-MoO_3 samples. In the spectra of W-C-3, W-C-4 and W-N-1, the absorption A and/or absorption B

could be observed.

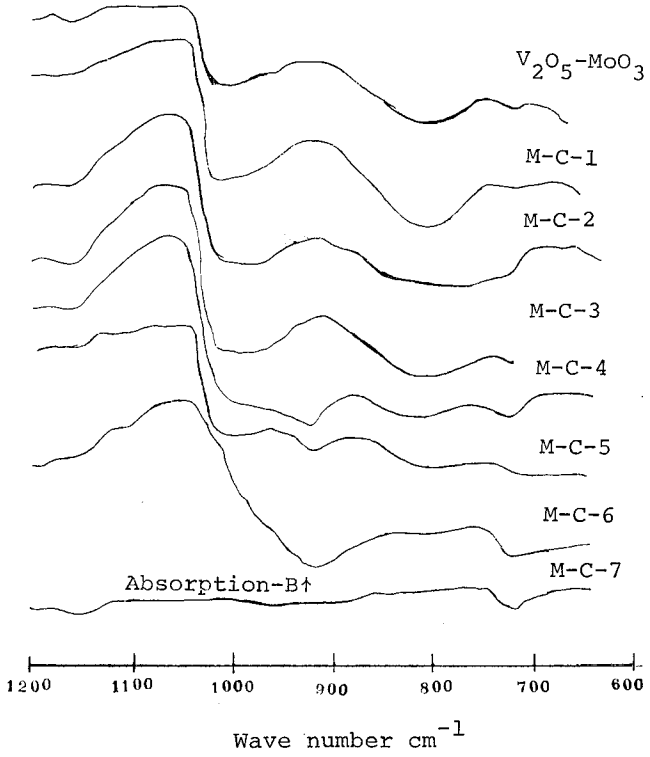


Fig. 8. Infrared absorption spectra of M-C series.

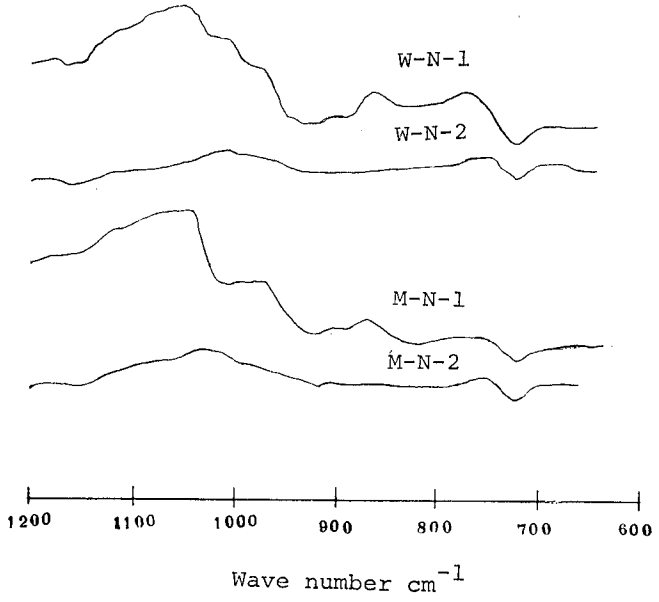


Fig. 9. Infrared absorption spectra of M-N and W-N series.

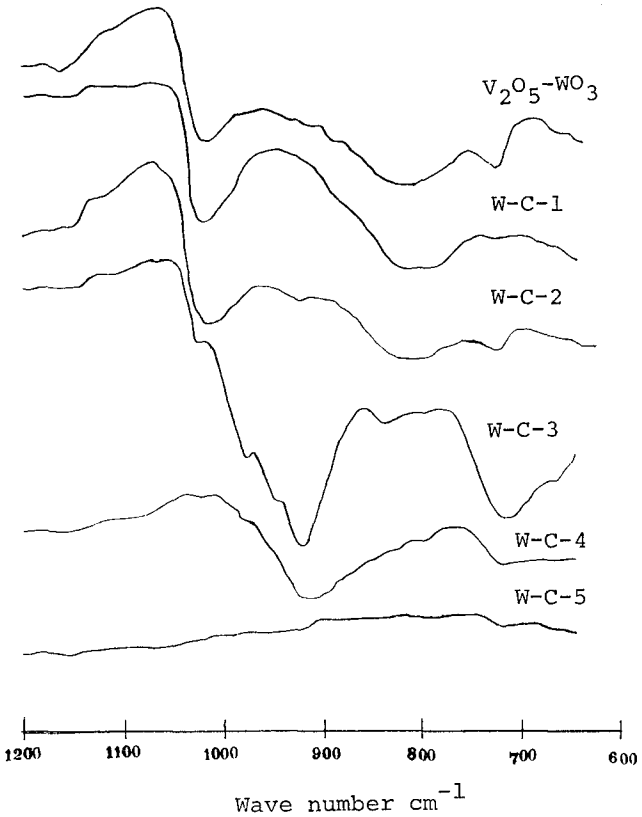


Fig. 10. Infrared absorption spectra of W-C series.

DISCUSSION

From the results of x-ray diffraction, it was found that V_2O_4 were partially formed in advance of $V_{12}O_{26}$, which is more oxidised state than V_2O_4, in the course of reduction of vanadium oxide catalysts.

The results mentioned above can be understood by remembering small diffusion constants of oxygen ions in these catalysts. The present authors studied previously the reduction rates of V_2O_5 and V_2O_5-MoO_3 (MoO_3 : 24.1 mol%) catalysts with H_2 or benzene and found that V_2O_5-MoO_3 was more reducible than V_2O_5, and that the rate determining step of the reduction was the diffusion process of oxygen ions in the crystal.[2,3,9] The obtained values of apparent diffusion constants had been

$$D_{V_2O_5} = 3.84 \times 10^8 \exp(-20100/RT)$$
$$D_{V_2O_5\text{-}MoO_3} = 7.06 \times 10^5 \exp(-12800/RT)$$

for V_2O_5 and V_2O_5-MoO_3 catalyst respectively.

These equations reveal also that V_2O_5-MoO_3 catalyst is more reducible than V_2O_5 catalyst at temperatures below 300°C.

Now, the formation of V_2O_4 in advance of $V_{12}O_{26}$ suggests that the diffusion

rate of oxygen ions in the crystal is not so rapid enough to cause homogeneous reduction through the whole crystal-phase, thus V_2O_4 is partially formed on the surface even though bulk phase of the crystal retains the crystal structure of V_2O_5.

It is interesting that though V_2O_5-MoO_3 catalyst is more reducible than V_2O_5 catalyst under this experimental condition, the V_2O_5-structure is retained untill more higher reduction temperature than in the case of V_2O_5, and that V_2O_4-structure which is formed in advance of $V_{12}O_{26}$ does not grow large. This can be explained by noticing the difference in diffusion constants of these samples. In the V_2O_5–MoO_3 catalysts, the diffusion of oxygen ions is easier than in V_2O_5 catalyst, thus oxygen ions may be furnished to the surface layer from inner part of crystal to prevent heterogeneous local reduction of surface layer.

There is no available value of the apparent diffusion constant for V_2O_5-WO_3 catalyst. However, the rate of the diffusion of oxygen ions has a correlation with the concentration of oxygen vacancy (or V^{4+} ions),[9] and the concentration of V^{4+} varies in order of $V_2O_5 < V_2O_5$-$WO_3 < V_2O_5$-MoO_3. Therefore, the reducibility and mobility of oxygen ions in this catalyst are assumed to be intermediate between V_2O_5-MoO_3 and V_2O_5. This assumption explains the results of x-ray diffraction measurements of V_2O_5-WO_3 catalyst.

The above explanation for the doping effect of MoO_3 or WO_3 is supported by the results of infrared spectroscopic measurements, too. The characteristic band due to V=O bond shifted to a longer wave length and grew broader by doping MoO_3 into V_2O_5. This fact means that the V=O bond of the V_2O_5-MoO_3 catalyst become more reactive than that of the V_2O_5 catalyst, and that as the result of this effect, the reducibility of the catalyst increases. The critical reduction conditions under which the characteristic V=O bond of the V_2O_5-structure is retained or not in the catalyst, are summarized in Table 3.

Table 3. The critical condition under which the V=O bond diminished.

Samples	By reduction with C_6H_{12}		By reduction with NH_3	
V_2O_5	at 204°C	○	at 350°C for 15 min	△
	at 262°C	×	at 350°C for 1 hr	×
V_2O_5-MoO_3	at 280°C	○	at 350°C for 15 min	△
	at 300°C	×	at 350°C for 1 hr	×
V_2O_5-WO_3	at 250°C	△	at 350°C for 15 min	△
	at 300°C	×	at 350°C for 1 hr	×

○ means that the absorption band by V=O bond could be observed clearly.
△ means that the weak absorption band by V=O bond could be observed.
× means that the absorption band by V=O bond could not be observed.

Table 3 reveals that the V=O bond is retained up to higher reduction temperature in order of $V_2O_5 < V_2O_5$-$WO_3 < V_2O_5$-MoO_3 at temperatures below 300°C.

As the V=O bond is associated with the characteristic crystal structure of V_2O_5, the retention of this bond reflects probably the stability of V_2O_5-structure.

It is noteworthy that in the V_2O_5-MoO_3 and V_2O_5-WO_3 catalysts, the samples,

which still had a crystal phase of V_2O_5, did not show the absorption band due to V=O bond (M-C-6 and W-C-4). This fact can be explained, if the infrared spectra reflected mainly the state of the thin surface layer of the samples. In the case of the V_2O_5 catalyst, the reduction proceeds heterogeneously in the surface and V_2O_4 is formed locally. Therefore, the V=O bond associated with V_2O_5-structure remains in the surface. On the other hand, in the case of V_2O_5-MoO_3 and V_2O_5-WO_3 catalysts, reduction proceeds homogeneously in the surface as mentioned above, so the V=O bond may diminish in the surface layer even if the V_2O_5-structure remains in the bulk phase.

In conclusion, the V_2O_5-catalyst are reduced to V_2O_4 via $V_2O_4+V_2O_5$ and $V_{12}O_{26}$ from the surface layer under the mild condition and by doping MoO_3 or WO_3 into V_2O_5 in the range of formation of solid solution, the crystal structure of V_2O_5 become more stable in spite of increase in its reducibility. It is presumed that this effect of MoO_3 or WO_3 correlates closely with its promotive action on V_2O_5-catalyst in oxidation reaction.

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